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Abstract

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Keywords

ion, lithium, materials, anode, method, template, batteries, catalytic, synthesis, nanostructures, cuo, different

Disciplines

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Synthesis of different CuO nanostructures by a new catalytic template method as anode materials for lithium-ion batteries†

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CuO powders composed of different rod-like clusters or dandelion-like nanospheres are prepared by a low-temperature thermal decomposition process of Cu(OH)₂ precursors, which are obtained via a catalytic template method. A tentative mechanism is proposed to explain the formation and transformation of different Cu(OH)₂ nanostructures. X-ray diffraction, thermogravimetric analysis, scanning electron microscopy, field-emission scanning electron microscopy, transmission electron microscopy, infrared spectra analysis, Brunauer–Emmett–Teller measurements, and galvanostatic cell cycling are employed to characterize the structures and electrochemical performance of these CuO samples. The results show that these CuO samples obtained after 500 °C calcination have a stable cycling performance with a reversible capacity of over 587 mA h g^{−1} after 50 cycles. The dandelion-like CuO electrode shows the best rate performance with a high capacity of 511 mA h g^{−1} at 4C.

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1. Introduction

The development of advanced portable electronics, electric vehicles and large-scale energy storage systems necessitates the demand for rechargeable lithium-ion batteries with higher energy density than ever before. Therefore, anode materials with higher specific capacity are desired for this purpose.^{1,2} Compared with a graphite anode with a capacity of 370 mA h g^{−1}, cupric oxide (CuO) has a much higher theoretical capacity of 670 mA h g^{−1}. Owing also to its advantages of low band-gap energy, nontoxic nature and affordable price, CuO has been investigated as a potential high energy anode material.^{3–8} However, CuO electrodes suffer from some drawbacks including poor electronic conductivity, low initial coulombic efficiency and large volume variation during discharge/charge processes, leading to material pulverization, poor cycling stability and rate capability. Various efforts have been made to solve these problems, including carbon-coating, reducing the particle size into nanometer scales and design of favorable particle morphologies. Recently, well-defined CuO microstructures with different dimensionalities such as nanoparticles,⁹

nanoribbons,¹⁰ nanowires,¹¹ nanorods,¹² nanoleaves,^{13,14} sisal-like film,¹⁵ urchin-nanostructure,¹⁶ and dandelion-like microspheres,^{17,18} have been synthesized by different methods. Nevertheless, most of these methods require relatively high temperature, time-consuming, and rather complicated procedures. Therefore, in this paper, we develop a simple wet-chemical process for the synthesis of different Cu(OH)₂ nanostructures at a low temperature without any surfactants and their subsequent transformation into CuO particles upon further heat treatment. By tailoring the reaction conditions, we can obtain CuO powders with different nano/micro-structures. As anode materials for lithium-ion batteries, these CuO electrodes exhibit good cycle performance and excellent rate capability.

2. Experimental

Different CuO nanostructures were synthesized by a simple wet-chemical process, in which the color of the reaction systems changes at different stages of this synthesis (Fig. 1). First, cupric acetate (Cu(AC)₂) was dissolved into ethylene glycol (EG) at 70 °C to obtain a light blue 0.1 M solution (Fig. 1a), and sodium hydroxide (NaOH) was dissolved in deionized water to obtain another solution (0.2 M). Then, different volumes of the Cu(AC)₂ solution were added drop-wise in the NaOH solution (100 ml) under constant magnetic stirring at room temperature. As soon as the Cu(AC)₂ solution was mixed with the NaOH solution, its color became bright blue (Fig. 1b). The volume of the Cu(AC)₂ solution added was 20, 30, and 40 ml, respectively, to obtain three different solutions. Afterwards, each blue solution was aged at

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room temperature for about 72 h without stirring to generate a light blue precipitate (Fig. 1c). The light blue precipitates were filtered and washed with distilled water for several times, and then dried at 70 °C in a vacuum oven for 12 h to obtain three dark brown powders (Fig. 1d). Subsequently, these powders were calcined at 500 °C for 6 h in air and cooled to room temperature. Finally, three black-colored powders were obtained.

The crystalline structures of the light-blue precipitates, dark-brown and black powders were characterized by X-ray diffraction (XRD) using a diffractometer (Rigaku TTR-III, Cu K α radiation) in the 2θ range from 10° to 70°. The thermogravimetric analysis (TGA) of the dark-brown powders was conducted on a thermal analyzer (Q5000IR, TA Instruments) in air from 30 to 750 °C at a heating rate of 5 °C min⁻¹. The morphologies and sizes of the dark-brown and black powders were observed by a scanning electron microscope (JSM-6390LA, JEOL) and a transmission electron microscope (H-800 Hitachi). Also, their specific surface areas were measured by Brunauer–Emmett–Teller (BET) method using nitrogen adsorption–desorption isotherms on a Surface Area Analyzer (SA3100, Beckman Coulter). The IR spectrums of the samples were studied by Fourier transform infrared spectrometers (MAGNA-IR750, Nicolet Instruments Co.).

It was proved that the electrochemical performance of the samples before the calcination is with a low coulombic

efficiency of about 48.9% (see ESI Fig. S1†). Thus, we mainly focused on the electrochemical properties of the CuO samples after the calcination. The electrochemical properties of the CuO samples obtained after the 500 °C calcination were evaluated in CR2032 coin cells with the CuO samples as the working electrodes and lithium metal as the counter electrode. The CuO electrode laminates on a copper foil were prepared with acetylene black (AB) as a conductive additive and poly(vinylidene difluoride) (PVDF) as a binder (CuO : AB : PVDF = 6 : 2 : 2 in weight). The laminates were punched into round discs with a diameter of 14 mm. The coin-cells were assembled in an argon-filled glove box (MBRAUN LABMASTER 130). The electrolyte was 1.0 M LiPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC) (EC : DEC = 1 : 1 v/v), and Celgard 2400 porous membrane was used as the separator. The cells were galvanostatically cycled at 25 °C on a multi-channel battery cycler (NEWWARE BTS-610) in the voltage range of 0.01–3.0 V. The impedance spectra of the cells were also measured on an electrochemical workstation (CHI 660A) in the frequency range of 0.005–100 kHz. In order to examine the morphologies of the CuO electrodes after cycle performance tests, these cells were eventually charged to 3.0 V and disassembled in a glove box. Then the CuO electrodes were analyzed by field-emission scanning electron microscope (FESEM, S-4800, Hitachi) after being washed with pure DEC to remove the electrolyte residue.

Fig. 1 The color change of the samples in the different stages: (a) Cu(AC)₂ dissolved into EG, (b) add Cu(AC)₂ solution into NaOH aqueous solution, (c) aging for 72 h, (d) before and after vacuum drying.

3. Results and discussion

3.1 Composition and structures of $\text{Cu}(\text{OH})_2$ and CuO

Fig. 2 gives the TGA curves measured under air atmosphere of three dark brown powders prepared by different conditions (Fig. 1d). At around 100 °C, the weight loss of the three dark brown powders is almost the same (about 2.39%), corresponding to the removal of the absorbed water. After that, there is a huge weight loss process from 100 to 300 °C for each sample, which may be attributed to the decomposition and removal of the organic ingredients. There is no weight loss above 500 °C for the three samples, indicating sufficient removal of the organic ingredients and the weight loss is about 6.02%, 10.32% and 14.30%, respectively. It is clear that with increasing the amount of $\text{Cu}(\text{AC})_2$ in the reaction systems, the proportions of organic ingredients in the dark brown powders also increases because more EG is brought into the reaction system that can form polymers and be left in the dried products. Also, based on the TGA result, the calcination conditions for the dark brown powders are chosen as 500 °C for 6 h in air.

Fig. 3 shows the XRD patterns of the powders obtained at different synthesis stages. The diffraction peaks of the light blue precipitate (Fig. 3a) can be indexed to the orthorhombic $\text{Cu}(\text{OH})_2$ (JCPDS no. 80-0656), while the diffraction peaks of the dark brown powder (Fig. 3b) obtained by drying the light blue precipitate at 70 °C can be indexed to monoclinic CuO (JCPDS card no. 45-0937). This indicates that the $\text{Cu}(\text{OH})_2$ powder can be converted into CuO at a rather low temperatures.¹⁹ Nevertheless, the peaks in Fig. 3a and b are broad, suggesting that the crystallinity of the as-prepared $\text{Cu}(\text{OH})_2$ and CuO is low. After the 500 °C calcination, all of diffraction peaks become sharper and can be perfectly indexed to the standard pattern of CuO crystalline structure (JCPDS card no. 45-0937) (Fig. 3c). Because no other peaks or broad peaks are detected, this powder should be a pure CuO phase. For the sake of simplicity, the CuO powders synthesized from different amount of 0.1 M $\text{Cu}(\text{AC})_2$

Fig. 3 XRD patterns of as-prepared samples with 40 ml $\text{Cu}(\text{AC})_2$ solution as an example: (a) the light blue precipitation, (b) the dark brown powder, (c) the black powders after the 500 °C calcination.

solution (20, 30, and 40 ml for 100 ml of 0.2 M NaOH solution) are named as C1, C2 and C3, respectively.

Typical SEM and TEM images of the as-prepared CuO nanostructures before and after the 500 °C calcination are shown in Fig. 4. Apparently, the amount of $\text{Cu}(\text{AC})_2$ in the reaction system has an important role to determine the nanostructures of the synthesized CuO samples. When the amount of $\text{Cu}(\text{AC})_2$ is little, the synthesized CuO (C1) is composed of many mono-dispersed nanorods with the diameter of about 20 nm and the length of from 400 nm to 800 nm (Fig. 4a and d). With increasing the amount of $\text{Cu}(\text{AC})_2$, the derived CuO (C2) changes its morphology from mono-dispersed nanorods to a mixture of nanorods and nanospheres (Fig. 4b and e). A self-assembly process must have occurred in the solution and each nanosphere with a diameter of about 500 nm is composed of many nanorods. However, with further increasing the amount of $\text{Cu}(\text{AC})_2$, only porous CuO nanospheres with a particle size ranging from 0.5 to 1.0 μm are obtained (Fig. 4c and f). After the 500 °C calcination, the particle morphologies of these three CuO powders (C1, C2 and C3) may change significantly. The morphology of C1 turns from mono-dispersed nanorods into irregular particles with particle sizes ranging from 10 to 20 nm (Fig. 4g). This change may be mainly due to the removal of some organic component that has formed the framework of C1 before the calcination. Since the inorganic content is low in C1 before the calcination, the nanorods can be easily broken into small particles during the calcination process. For C2 and C3 with more inorganic contents before the calcination, the obtained CuO powders still maintain the original morphologies after the calcination (Fig. 4h and i). More specifically, C3 consists of mono-dispersed spherical particles of about 500 nm in diameter, which are composed of many nanorods with an average diameter of about 10 nm. The nanorods become thinner from 20 nm to 10 nm after the calcination. These nanorods interweave together forming the cluster with an open porous structure after the organic

Fig. 2 TGA curves of the dark brown powders made from the different volume of $\text{Cu}(\text{AC})_2$ solution: (a) 20 ml, (b) 30 ml and (c) 40 ml.

Fig. 4 SEM and TEM images of the prepared CuO powders: (a and d) C1; (b and e) C2; (c and f) C3, before the 500 °C calcination. And TEM images of the corresponding CuO samples: (g) C1; (h) C2; (i) C3, after the 500 °C calcination.

framework is removed. Such a porous structure is able to facilitate electrolyte penetration into the electrode particles by providing a large contact area between the electrode material and electrolyte, so its electrochemical performance of the prepared materials can be improved.

To further verify the crystallization of the samples with and without high-temperature treatment, the HRTEM images of the C3 before and after the calcination was obtained and the result is shown in Fig. 5. It can be seen that there are only scattered domains with clear fringe lines before the calcination (Fig. 5a) while other areas show no clear fringe lines, indicating the existence of the amorphous CuO or possible organic components. After the calcination (Fig. 5b), the particles consist of very

clear fringe lines with a distance of about 0.25 nm between the lines, which is consistent with the distance of (002) lattice planes of CuO. This HRTEM result provides a clear evidence of the crystallinity change of CuO samples before and after the calcination.

3.2 Reaction mechanism of the catalytic template synthesis approach

By nitrogen adsorption–desorption measurements, the specific surface areas of the different CuO samples are shown in Table 1. The specific surface areas of C1, C2 and C3 before the calcination are 82.01, 97.79 and 116.60 m² g^{−1}, respectively. After the

Fig. 5 HRTEM images of the sample C3: (a) before and (b) after the 500 °C calcination.

Table 1 The specific surface areas of the different CuO nanostructures before and after the calcination

Sample	$V(\text{Cu}(\text{AC})_2, 0.1 \text{ M}) : V(\text{NaOH}, 0.2 \text{ M})$	Morphology	BET ($\text{m}^2 \text{g}^{-1}$)	
			Before calcination	After calcination
C1	2 : 10	Nanorods	82.01	9.78
C2	3 : 10	Nanorods–Nanospheres	97.79	15.52
C3	4 : 10	Nanospheres	116.60	29.92

calcination, the specific surface areas decrease substantially, being 9.78, 15.52 and $29.92 \text{ m}^2 \text{g}^{-1}$, respectively. The decreases are mainly due to the decomposition of the organic component that leads to the growth of CuO particles. For C3, more organic content (evidenced by the TGA analysis in Fig. 2) can suppress the particle growth of CuO so that its specific surface area is two to three times higher than those of C1 and C2.

In order to determine the nature of the organic component in C1, C2 and C3 before the calcination, the IR spectroscopy of C3 before and after the calcination was carried out and the

results are shown in Fig. 6. On the spectrum of C3 before the calcination (Fig. 6a), of the broad signal around 3428 cm^{-1} can be assigned to the vibrational mode of $-\text{OH}$ bond. The signals at about 1586, 1458 and 1388 cm^{-1} correspond to stretching vibrations of C–C (1586 cm^{-1}) and C–H (1458 and 1388 cm^{-1}) bonds, respectively, in a certain kind of polyethylene glycol (PEG).^{13,20} This result indicates that the monomer molecules EG can be polymerized into PEG molecules under the basic condition (NaOH) and likely with the help of catalytic effect of Cu^{2+} ions in the $\text{Cu}(\text{AC})_2$ solution. After the calcination, all characteristic signals for PEG have disappeared (Fig. 6b), suggesting that the organic component PEG has been removed completely.

On the basis of the above experimental results, a plausible formation mechanism diagram of CuO nanostructures is proposed as shown in Scheme 1. When $\text{Cu}(\text{AC})_2$ is dissolved into EG, one Cu^{2+} ion reacts with two EG molecules to form a complex with two positive charges. After the $\text{Cu}(\text{AC})_2$ solution is added with a NaOH solution, the functional groups of the complex are replaced with OH^- to form square-planar $[\text{Cu}(\text{OH})_4]^{2-}$ units with a homogeneous deep blue color.^{21,22} Subsequently, in the aging process, two reactions occur simultaneously. One is the polymerization of EG monomers to form poly(ethylene glycol) (PEG) under the conditions of basic environment and the catalytic effect of Cu^{2+} ions. Another reaction is the transformation of $[\text{Cu}(\text{OH})_4]^{2-}$ into orthorhombic $\text{Cu}(\text{OH})_2$ nanocrystallite that is a relatively stable phase.²² These $\text{Cu}(\text{OH})_2$ nanocrystallites are mainly adsorbed chemically on the PEG molecules by hydrogen bondings to form $\text{Cu}(\text{OH})_2$ –PEG units. Because PEG chain molecules can serve as a template to

Fig. 6 The IR spectrum of the sample C3: (a) before and (b) after the 500°C calcination. **Scheme 1** Schematic illustration of the growth of different CuO nanostructures under the different volume of $\text{Cu}(\text{AC})_2$ solution before the calcination.

Fig. 7 The discharge and charge profiles of CuO/Li half cells: (a) C1, (b) C2, and (c) C3 in the voltage range 0.01–3.0 V at a current density of 0.2C (1C = 670 mA g⁻¹). The cycle numbers are indicated in the graphs.

guide the growth of Cu(OH)₂ nanocrystallites to form Cu(OH)₂ nanorods. It is found here that the amount of the Cu(AC)₂ solution also plays an important role in the formation of Cu(OH)₂ nanostructures. Clearly, with increasing the amount of Cu²⁺ ions and EG molecules, Cu(OH)₂ nanorods–nanospheres composite structure starts to be formed instead of mono-dispersed Cu(OH)₂ nanorods. Eventually, the nanorods are self-assembled into roughly mono-dispersed nanospheres.

3.3 Electrochemical properties of CuO samples

The as-prepared CuO samples are used as anode materials for lithium-ion batteries and the voltage profiles of different cycles are shown in Fig. 7. All three electrodes exhibit similar voltage profiles. Taking C3 as an example, in the first discharge process,

there is a voltage drop from 2.25 V to 1.75 V, which can be attributed to the reduction reaction from CuO to the intermediate composite copper oxide phase Cu_{1-x}^{II}Cu_x^IO_{1-x/2}. Then, an obvious voltage plateau at about 1.3 V appears, which corresponds to the Cu_{1-x}^{II}Cu_x^IO_{1-x/2} to Cu₂O. And another obvious voltage plateau at about 0.8 V appears, which corresponds to the conversion reaction that Cu is driven out from the lattice to form nano-Cu clusters in a Li₂O matrix, *i.e.* Cu₂O + 2Li → 2Cu + Li₂O.^{18,23–26} The sloping part below 0.8 V can be attributed to the formations of a gel-like film and the solid electrolyte interphase films on the surface of the CuO particles. During the subsequent charge step, only two inclined plateau near 1.6 V and 2.5 V can be observed, corresponding to the process of nano-Cu to Cu₂O and the partial oxidation of Cu₂O to CuO, respectively. The initial discharge capacities of the three samples are 1072,

Fig. 8 Electrochemical properties of CuO samples: (a) cycle performance of the electrodes at a current rate of 0.2C; (b) rate performance of the electrodes at different current density.

1258 and 1240 mA h g^{-1} , respectively, which are greater than the theoretical capacity (670 mA h g^{-1}). The excessive capacities are contributed mainly by the formation of a polymeric gel-like film but a small portion of it is also contributed by the conducting additive acetylene black (AB) and possibly interfacial lithium storage.²⁷ The initial coulombic efficiency of these electrodes is 57.2%, 52.4%, 62.8% and the initial capacity loss is 39.6%, 38.7%, and 33.4%, respectively. These differences in initial discharge capacity, coulombic efficiency and capacity loss are mainly due to the differences in specific surface area

and the microstructure of the three CuO samples. After 50 cycles, the discharge capacity of three samples is 537, 542 and 587 mA h g^{-1} , respectively.

The cyclic voltammograms of the three CuO electrodes (Fig. S2†) also show similar results with the cathodic and anodic peaks appearing at corresponding voltages. Also, the calculated initial capacity loss derived from the CV measurements of these electrodes is 42.9%, 42.3%, and 36.4%, respectively, which are consistent with the above trend measured from galvanostatic cycling (39.6%, 38.7%, and 33.4%, respectively).

The cycling performance and rate capability of the CuO electrodes are shown in Fig. 8. All of the electrodes show stable cycling performance and maintain high coulombic efficiency with an average value of about 97.5% after the first cycle (Fig. 8a). The stable cycling performance of these samples comes from their unique microstructures. Among these three samples, C3 exhibits the best cycling performance that a specific capacity of 587 mA h g^{-1} can be obtained after 50 cycles. This result should be attributed to its unique hierarchical architecture that possesses the most open structure and the largest specific surface area among the three samples. Its large specific surface area can help a quick infiltration of electrolyte and shorten the diffusion lengths for both lithium ions and electrons. Thus, compared with C1 with irregular nanoparticles, C3 with porous mono-dispersed nanospheres can not only offer more sites for Li^+ accommodation, but also help to accommodate the volume change during the charge/discharge process. Fig. 8b shows the rate performance of the CuO electrodes at various current densities from 0.2C to 4C. It can be easily seen that C3 also displays the best rate performance with a high

Fig. 9 Impedance spectra of CuO/Li cells at the end of charge after 50 cycles at a current density of 0.2C: (a) C1, (b) C2 and (c) C3.

Fig. 10 SEM images of the fully charged CuO electrodes after 50 cycles at a current density of 0.2C: (a) C1, (b) C2 and (c) C3.

capacity of 796, 695, 620, 553, and 511 mA h g⁻¹ at 0.2C, 0.5C, 1C, 2C, and 4C, respectively. When the charge rate returns to 0.2C, it can still deliver a high reversible capacity of 623 mA h g⁻¹. For C2, its rate performance at a low rate (0.5C and 1C) is similar to C3, but the discharge capacity is 524 and 463 mA h g⁻¹ at 2C and 4C, respectively, which are lower than those of C3. For C1, the discharge capacities are markedly lower than those of C3 and C2. All these results show that C3 displays both outstanding cycling performance and rate capability.

The impedance spectra of the C1, C2 and C3 electrodes at the end of the charge in the 50th cycle are shown in Fig. 9. The plots are similar to each other in shape, with two overlapped depressed semicircles in the high and intermediate frequency regions and a straight line in the low frequency region. The small semicircle in the high frequency region, which may be contributed from the metallic lithium electrode side, while the semicircle in the intermediate frequency region can be clearly observed, which can be assigned to the charge-transfer impedance at CuO electrode/electrolyte interface. Obviously, the impedance in C1 electrode is the largest, followed by C2 electrode and the smallest is C3 electrode. Thus, the open microstructure of the electrode is advantageous to reduce the charge-transfer impedance. Therefore, the C3 electrode shows the most excellent electrochemical performance.

The microstructures of these fully charged CuO electrodes are investigated after the cycling performance test (Fig. 10). It is found that in Fig. 10a, there are some spherical particles and rod-like particles ranging from 100 nm to 240 nm in size distributed in the C1 electrode film, which are much different from the original nanorods morphology of CuO in as-calcined C1. This difference is mainly due to the pulverization and agglomeration of the CuO nanorods caused by the large volume change during electrochemical cycling process. For the C2 electrode (Fig. 10b), in addition to forming the small spherical particles that are similar to C1 electrode film, there are some large spherical particles of about 0.55 μ m in size, which still maintain the size of the spherical clusters in original C2. But the particles here are no longer porous due likely to the filling of the pores by residual electrolyte or related products produced during electrochemical cycling.²⁸ For the C3 electrode (Fig. 10c), although the pore size becomes smaller than in the as-calcined C3, it still maintains the open structure composed by a large number of nanorods. Obviously, the more open structure and larger specific surface area of C3 can effectively alleviate the volume and stress changes during the cycling.

4. Conclusions

In this paper, we have developed a new and simple catalytic template method and successfully prepared the rod-like or dandelion-like Cu(OH)₂ and CuO particles. The CuO samples are used as anode materials for lithium-ion batteries and show stable cycling performance with improved rate capability. In particular, the dandelion-like CuO sample exhibits the best electrochemical performance with high rate capability and reversible cycling performance. This new catalytic template approach also provides a way to prepare other metal oxides with

unique nanostructures as the anode materials for high performance lithium-ion batteries.

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